

# PREPARATION AND CHARACTERIZATION OF Co-Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> CATALYSTS

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## INTRODUCTION

Hydrocracking catalysts are bifunctional catalysts having both hydrogenation-dehydrogenation function and an acidic function. Proper balancing of the two functions plays a prominent role in deciding the performance of the catalyst for application in hydrocracking [1]. The cracking function is provided by an acidic support, whereas the hydrogenation-dehydrogenation function is provided by metals. The acidic support consists of (a) amorphous oxides (e.g., silica-alumina), (b) a crystalline zeolite (mostly modified Y zeolite) plus binder (e.g., alumina), or (c) a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support. The metals providing the hydrogenation-dehydrogenation function can be noble metals (palladium, platinum) or non-noble metal sulfides from group VIA (molybdenum, tungsten) and group VIIA (cobalt, nickel). These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation. The ratio between the catalyst's cracking function and hydrogenation function can be adjusted to optimize activity and selectivity. For a hydrocracking catalyst to be effective, it is important that there be a rapid molecular transfer between the acid site and hydrogenation sites in order to avoid undesirable secondary reactions. Rapid molecular transfer can be achieved by having the hydrogenation sites located in the proximity of the cracking (acid) sites [2]. Catalysts with amorphous support are in commercial use, primarily where maximizing the production of middle distillates or conversion to lube oil blending stock is the objective [3,4]. Amorphous hydrocracking catalysts contain primarily amorphous silica-alumina [5]. Other amorphous supports reported are titania-zirconia, silica-alumina dispersed in alumina, alumina-boria, and other acidic mixed oxides. Hydrocracking catalysts containing fluorinated inorganic oxides as supports have also been reported [6]. In this research work a series of CoMo-silica-alumina amorphous base hydrocracking catalysts was prepared by impregnation method. The amorphous silica alumina support was prepared in the laboratory by co-precipitation method. The effect of order of impregnation of cobalt and molybdenum on the catalyst activity was studied by specific characterization methods and model compounds reactions. In addition,  $\gamma$ -alumina and Y-zeolite based catalysts were also prepared and studied for comparison purposes.

## EXPERIMENTAL

**Catalyst Preparation:** A series of silica-alumina supported CoMo hydrocracking catalysts were prepared by impregnation method. The order of impregnation of cobalt and molybdenum was varied. For catalyst HC-1, molybdenum was impregnated first and then cobalt was loaded. In catalyst HC-2, this order was reversed. On the other hand, simultaneous impregnation of cobalt and molybdenum was adopted for the preparation of catalyst HC-3. All catalysts were calcined at 500 °C for three hours in a stream of dry air. The silica-alumina supports were also prepared in the laboratory by co-precipitation method. In addition,  $\gamma$ -alumina and 50% mixture of  $\gamma$ -alumina and commercial Y-zeolite were also used as supports. Catalyst HC-4 was prepared by using commercial acidic alumina supplied by Aldrich. For the preparation of catalyst HC-5, a 50% mixture of commercial  $\gamma$ -alumina (Aluminum Company of America) and Y-zeolite (CATAL, UK) was used. Commercial  $\gamma$ -alumina and Y-zeolite were dried at 250 °C before using as catalyst support.

**Catalyst Characterization:** The catalysts samples were characterized by temperature-programmed desorption (TPD) of ammonia, temperature-programmed reduction (TPR), and temperature-programmed sulfiding (TPS). The details of the measurements are given elsewhere [7]. The elemental composition of the catalysts was measured by ICP. Surface area (BET method) and pore volume was measured by Quantachrome (NOVA 2000).

**Catalyst Evaluation:** The prepared hydrocracking catalysts were evaluated for HDS and cracking activities using thiophene and cumene as model compounds, respectively. The activity measurements were conducted in a pulse type micro reactor. The detailed experimental procedures are given elsewhere [7].

## RESULTS AND DISCUSSION

Some of the physico-chemical properties of the prepared catalysts are given in Table 1. It was observed that the surface area of the catalyst was reduced as compared with the blank support, after the impregnation of the metals. This could be due the pore blocking by cobalt and molybdenum in the catalysts. This was also evident from the reduction in pore volume of the catalysts in comparison with the respective support. However, the reduction in surface area for

the  $\gamma$ -alumina-based catalyst (HC-4) was not as pronounced as in the case of synthesized silica-alumina-based catalysts. Similarly, the surface area of HC-5 was comparable with the average surface area of the respective support.

**Temperature-Programmed Reduction:** The results of temperature-programmed reduction of silica alumina and zeolite based catalysts are given in Figure 1. Almost all the catalysts show a multiple peak reduction behavior. The first reduction appear in the region of 300 to 500 °C. The variation in the peak temperature was attributed to the differences in the metal support-interactions and multiple peak pattern might be due to the presence of molybdenum at different sites of the support. The highest reduction temperature was observed for HC-1 (peak at 363 °C). On the other hand, HC-5 reduced at minimum temperature in the series giving a shoulder at 397 °C with the main peak at 462 °C. It was also observed that catalyst prepared by simultaneous impregnation of metals (HC-3) reduced at lower temperature (431 °C) as compared with its homologues. The reduction temperature indicates the metal-support interaction, which in turn influences the HDS activity of the catalyst.

**Temperature-Programmed sulfiding:** The results of temperature-programmed sulfiding are given in Figure 2. The TPS profiles are similar to the molybdenum containing commercial catalysts. The upper curve represents the UV-detector signal, which monitors the hydrogen sulfide concentration, where the positive peak means the production of hydrogen sulfide and the negative peak means consumption. The lower curve is a response of the TCD, which monitors the hydrogen concentration, and the positive peak in this case indicates the consumption of hydrogen. The TPS profile can be divided into four regions. In the region I (25 to <100 °C) the positive peak in UV signal is due to the desorption of hydrogen sulfide, which was mainly adsorbed physically during stabilization at room temperature. The desorption of hydrogen sulfide is followed by a low-temperature sulfiding in region-II (below 200 °C). No hydrogen is consumed in this region as noticed in the lower curve. Arnoldy et al. [8] showed in their study that sulfiding in this region occurs by simple O-S exchanges on  $\text{Mo}^{+6}$ . In region-III, hydrogen sulfide is produced as a sharp peak, coupled with the consumption of hydrogen. The sharpness of the peak points to a chemically well-defined surface compound. In this region  $\text{Mo}^{+6}$ -S bond is breaking down and the free sulfur is reduced so the hydrogen sulfide is produced. This peak appeared at 134 °C for HC-5 whereas, for HC-2 it is at 218 °C. The sharpness of the peak in catalyst HC-2 also indicates the homogeneous distribution of molybdenum over the catalyst support. Note that in this sample, molybdenum was impregnated after the cobalt loading. While, catalyst HC-1 gave relatively broad peak at 199 °C in which the order of impregnation was reversed. This gives some indication that there may exist some competition between the metal ions being impregnated over the support. High temperature sulfiding (region-IV) is taking place above 250°C in all cases. In this region, most of Mo ions are already in  $\text{Mo}^{+4}$  state, sulfiding can be described mainly as O-S exchange on  $\text{Mo}^{+4}$  ions. Sulfiding appears to be completed at about 800°C in all cases. In this region, HC-4 gave a shallow peak as compared to other catalysts. On the other hand, HC-2 and HC-3 showed maximum consumption of  $\text{H}_2\text{S}$  in this region.

**Temperature-programmed Desorption:** Total acidity of the silica alumina and zeolite based catalysts, measured by TPD of ammonia is given in the Table 2. Figure 3 shows the TPD curves of these catalysts. The total acidity (Bronsted and Lewis) measured was in the range of 0.3 to 0.8 m mole/g. For the catalysts HC-1, -2 and -3 the order of impregnation of cobalt and molybdenum appears to be playing a role in determining the acidity. It was found to be highest in the case of simultaneous impregnation of the metals. Quite interestingly, the total acidity was lower for the catalyst containing Y-zeolite (HC-5) as compared with some of the silica-alumina based catalysts. This indicates that there might be more Lewis acid sites in silica-alumina based catalysts as compared with zeolite containing catalyst. The cracking of cumene will give more information about the acidic properties of the catalysts.

**Catalytic Activity:** Hydrocracking of cumene was performed to evaluate the cracking property of the catalysts. The results of cumene cracking are given in Figure 4. Maximum cracking activity was observed for HC-5 (zeolite based). This higher cracking activity was attributed to the presence of Y-zeolite in the catalyst. HC-3 catalyst showed maximum total acidity (0.765 m mol/g), but it gave lower cumene cracking (46.7%) as compared to HC-5 (97.9% cumene conversion). It was observed that total acidity measured by TPD of ammonia was not well correlating with the cracking of cumene. This indicates that Lewis acid sites are contributing more to the acidity measurement as compared to the Bronsted acidity (for silica-alumina catalysts) which is required for cracking activity. In the silica-alumina based catalyst series, maximum cumene cracking was found for HC-1 (78.5%) whereas, HC-2 gave minimum conversion (34.3%). This shows that the order of impregnation of cobalt and molybdenum plays an important role in the cracking activity of cumene. The cracking activity was higher when molybdenum was impregnated first and lower in the case where cobalt was impregnated first followed by molybdenum. Total acidity was also lower for HC-2 as compared with that of HC-1. These results show that cobalt is interacting with the acid sites and blocking them so that

the total acidity was decreased. This requires further investigations in terms of metal-acid-sites interactions.

The hydrodesulfurization of thiophene was performed to measure the HDS activity of the catalysts. Figure 5 shows the results of HDS of thiophene at different temperatures. The highest HDS activity was found in the case of HC-4 (alumina based catalyst). On the other hand, minimum HDS activity was observed for HC-1. Here also the order of impregnation of metals plays a role. In the series of silica-alumina based catalysts, the highest HDS activity was found for HC-3. In the catalyst cobalt and molybdenum were impregnated simultaneously. A trend was observed between the HDS activity and the reduction temperature measured by TPR. It was found that at lower reduction temperature higher HDS activity occurred. Figure 6 shows the correlation of thiophene conversion versus peak temperature of TPR profile. For catalyst HC-5 the average of the two peaks was used for correlation curve.

## CONCLUSIONS

The order of impregnation of cobalt and molybdenum over silica-alumina based hydrocracking catalysts plays an important role in terms of catalyst activity. Maximum cracking activity was found for the catalyst prepared by impregnating molybdenum first and then cobalt in the second step over silica-alumina support. Temperature programmed methods were successfully utilized for the characterization of the prepared hydrocracking catalysts. A trend was observed for the HDS activity of the hydrocracking catalysts and reduction temperature measured by TPR method. Catalysts reducing at lower temperature performed better for HDS activity.

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**Table 1. Physico-chemical properties of CoMo-supported hydrocracking catalysts**

Catalyst Code	Support	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	CoO (wt %)	MoO <sub>3</sub> (wt %)
HC-1	SA*	145	0.20	3.89	13.2
HC-2	SA	124	0.24	4.86	14.4
HC-3	SA	183	0.19	4.10	15.1
HC-4	γ-Alumina**	140	0.23	5.35	13.7
HC-5	γ-Alumina + Y-Zeolite**	280	0.29	3.74	14.5

\* Silica-Alumina support prepared in the laboratory; surface area 376 m<sup>2</sup>/g pore volume 0.34 cc/g

\*\* Acidic alumina, surface area 140 m<sup>2</sup>/g from Aldrich

\*\* γ-Alumina surface area 216 m<sup>2</sup>/g from Aluminum Company of America  
Y-Zeolite surface area 515 m<sup>2</sup>/g from CATAL, UK.

**Table 2. Results of TPD analysis**

Catalyst	Acidity (m mol/g)
HC-1	0.589
HC-2	0.288
HC-3	0.765
HC-4	0.320
HC-5	0.413

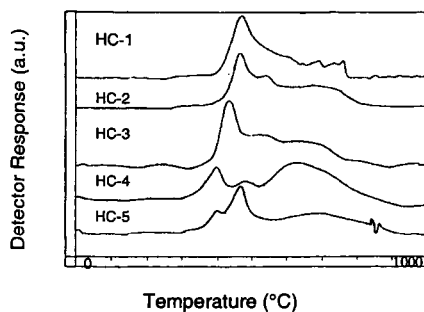


Figure 1. TPR profiles of CoMo-supported hydrocracking catalysts.

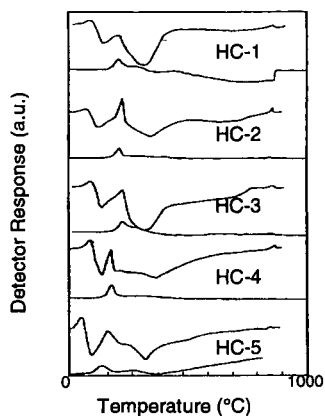


Figure 2. TPS profiles of CoMo-supported hydrocracking catalysts.

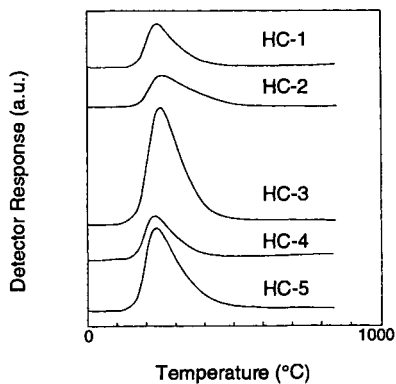


Figure 3. TPD profiles of CoMo-supported hydrocracking catalyst.

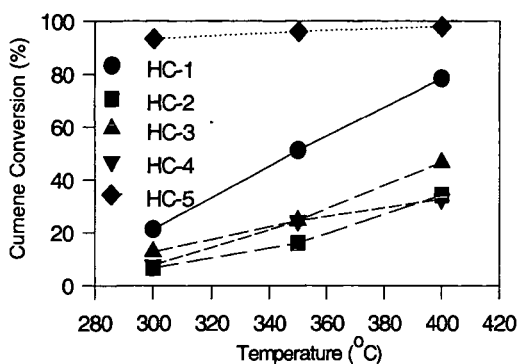


Figure 4. Cumene cracking activity at different temperatures.

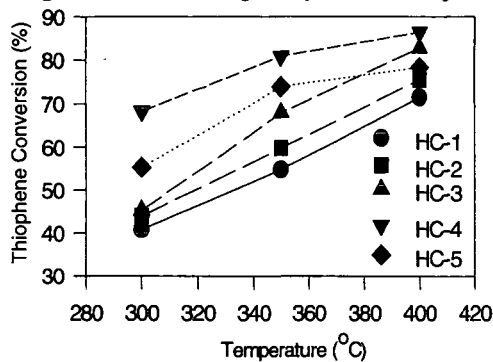


Figure 5. Thiophene HDS activity at different temperatures.

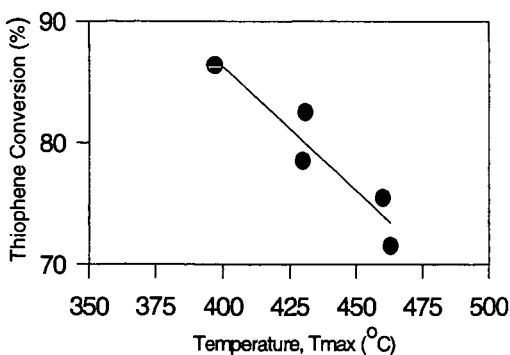


Figure 6. Correlation of thiophene conversion versus TPR Tmax